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Short communication

Inter-wall bridging induced peeling of multi-walled carbon nanotubes during tensile failure in aluminum matrix composites

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ABSTRACT

In situ scanning electron microscopy (SEM) observation of a tensile test was performed to investigate the fracturing behavior of multi-walled carbon nanotubes (MWCNTs) in powder metallurgy Al matrix composites. A multiple peeling phenomenon during MWCNT fracturing was clearly observed. Its formation mechanism and resultant effect on the composite strength were examined. Through transition electron microscopy characterizations, it was observed that defective structures like inter-wall bridges cross-linked adjacent walls of MWCNTs. This structure was helpful to improve the inter-wall bonding conditions, leading to the effective load transfer between walls and resultant peeling behaviors of MWCNTs. These results might provide new understandings of the fracturing mechanisms of carbon nanotube reinforcements for designing high-performance nanocomposites.

1. Introduction

Carbon nanotubes (CNTs), due to their unique one or multi-layer tubal graphene structure, have attracted great attention for structural and functional uses (Iijima, 1991). Excellent mechanical properties, high aspect ratio, large surface area and light weight, make CNTs ideal fibrous reinforcements for composite materials. In the past 20 years, CNT reinforced composites in various matrices have been studied intensively for applications as the next generation strong structural materials (Popov, 2004; Bakshi et al., 2010). Up to date, however, the reported mechanical properties of CNT reinforced composites are still much lower than expected. The understanding of the fracturing behavior of CNTs in composites is basically essential to the design of high-strength composite materials (Bakshi et al., 2010; Boesl et al., 2014; Gallego et al., 2012). From the in situ studies on individual multi-walled carbon nanotubes (MWCNTs) (Yu et al., 2000) and MWCNTs in composites (Yamamoto et al., 2008), MWCNTs were clearly observed in a 'sword-in-sheath' fracturing mode: the outermost wall of MWCNTs was fractured and the inner walls were pulled out. Due to the low inter-wall shear strength (IWSS) (Yu et al., 2000; Soule and Nezbeda, 1968), applied load was hard to transfer to the inner walls of MWCNTs during failure. It led to a low load transfer efficiency and resultant mild strengthening or toughening effect in CNT reinforced composites (Yamamoto et al., 2008).

Recently, some studies (Peng et al., 2008; Byrne et al., 2009) suggested that the introduction of defective structures, such as inter-wall sp^3 bridging, could lead to the enhancement of IWSS of MWCNTs. They also reported that the inter-wall load transfer improves with increasing the defect density (Peng et al., 2008). These results suggested that a noticeable load transfer strengthening effect might be achieved in CNT reinforced composites through the design of CNT structure, especially defects. In this study, a high-defect-density MWCNT synthetized by the chemical vapor deposition method was used to reinforce pure Al matrix. An in situ scanning electron microscopy (SEM) observation of tensile CNT/Al composite was applied to examine the MWCNT fracturing behavior during composite failure. A multiple peeling fracturing phenomenon was detected from the in situ SEM observations. Its formation mechanism was examined, and its effect on the mechanical properties was discussed.

2. Experimental methods

The CNT/Al composite was fabricated through a powder metallurgy route. Pure Al and 0.6 wt.% MWCNTs (commercially named VGCF-H, ∼100 nm in diameter, ∼15 μm in length, with fracture strength of ∼5 GPa, density of 2.1 gcm^{-3}, purchased from Shawa

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Denko Co., Japan) powders were mixed by Al_2O_3 media balls (ball to powder massive ratio of 1:10) using a rocking milling machine (Seiwa Giken) for 4 h. The milled powder mixture was subsequently consolidated by sparking plasma sintering (SPS) and the following hot-extrusion. SPS was conducted by using an SPS system (SPS-1030S, SPS Syntex) at a sintering temperature of 823 K held for 0.5 h at a pressure of 30 MPa under a vacuum of 5 Pa. Before hot extrusion, the as-sintered billet was preheated at 773 K for 180 s under an argon gas atmosphere. The billet was then immediately extruded using a 2000 kN hydraulic press machine (SHP-200-450, Shibayama). The extrusion ratio and the ram speed were 12:1 and 0.5 mm/s, respectively. The morphologies of raw CNT and the extruded CNT/Al composites were examined by transmission electron microscopy (TEM, JEM-2010, JEOL). TEM samples of the composites were fabricated with a focused ion beam (FIB, HITACHI FB-2000A) system. The defect density of MWCNTs was investigated by Raman spectroscopy (Microscopic Laser Raman Spectrometer, LabRAM ARAMIS).

The in situ tensile test of CNTs/Al composite was operated inside a field emission SEM (FE-SEM, JEM-6500F, JEOL). The sample was machined from the extrusion rod into a flat dog-bone shape with gauge length of 10 mm. The effective cross-section area is 2 mm in width and 1 mm in thickness. The sample was placed into the two clamping heads of the tensile machine, and then loaded with a tensile speed of 5 μm/s. Tensile test was manually paused during the tensile test. During the pauses, the displacement was held on and SEM photos were captured. Tensile loading was then restarted to the next pause point until the sample was fractured. Furthermore, in order to accurately evaluate the tensile strength at room temperature, a regular tensile test was undertaken by using a universal testing machine (AUTOGRAPH AG-I 50 KN, Shimadzu Co. Ltd., Japan) at a strain rate of $5 \times 10^{-4}\,s^{-1}$. Tensile specimens with gauge length of 15 mm and diameter of 3 mm were machined from the extruded rods. The average tensile strength was measured from five specimens. The tensile axis of both in situ and standard tensile tests was parallel to the extrusion direction.

3. Results and discussion

Fig. 1 shows the TEM observations of raw MWCNTs at different magnifications. CNT exhibited a large aspect ratio (length to diameter ratio). Regular CNT walls with a spacing of 0.34 nm were clearly observed (Fig. 1b). Many structure defects were also observed. The high-resolution TEM (HRTEM) image (Fig. 1c) shows the morphology of a typical defect. These defective walls (non-parallel to CNT axis) like a bridge cross-linked the adjacent regular walls (parallel to the axis). Raman spectra have been used for characterizing the defect density of CNTs by many studies (Chen et al., 2014; Jiang et al., 2012). The peaks at ∼1350 cm^{-1} and ∼1572 cm^{-1} correspond to a typical D-band (defect) and G-band (graphite), respectively. The relative intensity between the two peaks (I_D/I_G) is known to provide information about the defect density of the internal CNTs. I_D/I_G was measured as ∼0.1 for the present MWCNTs.

Fig. 2 shows the morphology of MWCNT incorporated in AMCs. CNT was well contacted with Al matrix via a clean interface, and no other interface phases could be observed (Fig. 2a). It suggested that CNTs were stable in the present processing conditions. As a result, the inter-wall bridging structures from raw MWCNTs (Fig. 1) were introduced into the composite, as indicated by the arrows in Fig. 2b. A typical defect consisting of ∼30 walls (the frame in Fig. 2b) is shown in Fig. 2c. These walls were non-parallel to the axis direction and cross-lined with other walls, which were schematically shown in Fig. 2d.

The fracturing of MWCNTs in AMCs in different tensile test stages is shown in Fig. 3. Fig. 3a exhibits the tensile stress–strain curve marked with paused Stage B–E which are shown in Fig. 3b–e, respectively. During the yielding process (from start to Stage A in Fig. 3a) of AMCs, little microstructure change of the composite could be observed. After yielding stage, cracks grew and expanded in the matrix, CNTs were exposed and restrained the growing tendency of the crack (Fig. 3b). As the tensile displacement was increased, CNTs began to fracture one by one (Fig. 3c). The outer walls of the CNT designated as (1) has fractured and some debris is touched on the broken area. The fresh inner nanotube of CNT (1) is exposed with a decreased out-diameter as an arrow indicated in Fig. 3c. Spontaneously, CNT (2) is experiencing a peeling fracture process with multi-fractured-stages. From the outer-diameter gradient of the left CNT segment, it suggests that, like CNT (1), CNT (2) initially fractured at the outer layer, and the wall-breaking vertically grew into the CNT with some depth. Then the fracturing position shifted to another position which was some axial distance away from the previous fracturing point. This peeling behavior has repeated twice along the tensile direction with CNT (2), leaving three rod stages with different out-diameters (Fig. 3c). The peeling behavior moved on until all the walls were fractured. After tensile test, ruptured CNTs were observed on the fracture surface (Fig. 3d and e). CNT (3) exhibited a multiple peeling morphology and CNT (4) showed only one-time peeling. Moreover, at the peeling positions, peeling slopes with gradually changed CNT outer-diameter were often observed as arrows indicated in Fig. 3c–e. With CNT (3), there was a long slope between the two stages with outer-diameter of ∼230 and ∼50 nm. The morphology schemes of CNT (3) and (4) are shown in Fig. 3f. The existence of peeling slopes suggested that wall fracturing was transferred from outer to inner walls through the bonding structure between walls. These structures, which were non-parallel to the axis direction, were most probably induced by the bridging walls observed in MWCNTs (Fig. 2).

Because of the effectively interfacial bonding between the outermost wall of CNTs and the matrix Al (Fig. 2a and b), a shear stress (Cox, 1952) can be formed and help to transfer load to the outermost wall during composite failure. In the case of CNT fracture observed in this study (Fig. 3), tensile stress applied in the outermost wall must have exceeded the wall strength, so the interfacial strength (τ) should be larger than a critical interfacial strength (τ_c). τ_c can be obtained from the shear-lag theory (Kelly and Tyson, 1965) and expressed as

$$\tau_c = \frac{D \cdot \sigma_f}{2L} \tag{1}$$

where D, L and σ_f are the diameter (∼100 nm), length (∼10 μm after milling) and the fracture strength of MWCNTs, respectively. In this study, σ_f of MWCNT was provided as ∼5 GPa by the manufacturer. It was basically coincident with in a similar CNT type, σ_f of which was reported as 4 GPa (Esawi et al., 2010). Therefore, τ_c was estimated as 25 MPa. It suggested that τ of the present CNT-Al system was larger than 25 MPa. As the displacement increased after the outermost wall was ruptured, the load was further transferred to the inner walls. Similarly, if the inter-wall strength (τ_{iw}) is larger than a critical value, the inner wall will be ruptured. In this case, the critical inter-wall strength could be regarded as the same value with τ_c (25 MPa), because of the same values of L and σ_f, and a little decrease (the thickness of two walls, 0.68 nm) of D for the inner wall. In a low defect-density MWCNT, however, the van der Waals (vdW) force between adjacent walls was reported as ∼0.45 MPa (Yu et al., 2000; Soule and Nezbeda, 1968). It suggests τ_{iw} was farther below the critical value, resulting in the previously observed pulling-out of inner walls or the outermost-wall fracture (Yu et al., 2000). Due to the existence of bridging walls, τ_{iw} was greatly enhanced, even larger than τ_c, leading to the rupture of inner walls which was observed in this study. Moreover, stress concentration was easy to happen at the position of bridging walls due to their structure